Preparation and Structure of Dinuclear Vanadium(III) Complex Triply Bridged by Three Different Groups

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A new dinuclear vanadium(III) complex, $[V_2(bza)(OH)(tphpn)(H_2O)_2]Cl_3$, was prepared and its structure was characterized by X-ray crystallography, where bza is benzoate and tphpn is an anion of *N*, *N*, *N*', *N*'-tetrakis(2-pyridylmethyl)-2-hydroxy-propane-1,3-diamine.

A variety of dinuclear complexes of manganese and iron have been studied in relation to the biological function of these metal ions. Several dinuclear vanadium(III) complexes have also been examined with regard to the vanadium in tunicate blood cells.[1]

From the viewpoint of coordination stereochemistry, vanadium(III) ion has more flexibility in its coordination geometry than manganese and iron ions. For example, heptacoordination is not very rare for vanadium(III) complexes and three possible polyhedrons of the heptacoordinate structure (such as pentagonal bipyramid,[2] capped trigonal prism,[3] and capped octahedron[4]) have all been realized. The heptacoordinate dinuclear vanadium(III) complexes so far obtained are $[V_2(dpot)_2]^{2-}$ [2] (dpot = 1,3-diamino-2-propanol-*N*,*N*,*N*',*N*'-tetraacetate) and $[V_2(hedtra\text{-}H)_2]^{2-}$ [5] (hedtra = *N*-hydroxyethyl-ethylenediamine-*N*,*N*',*N*'-triacetate), which contain two equivalent multidentate ligands. Here we report the preparation and structure of a new type of mixed-ligand dinuclear vanadium(III) complex consisting of two heptacoordinate monomeric units.

The dinucleating septidentate ligand, Htphpn, was obtained from 1,3-diamino-2-hydroxypropane and 2-picolyl chloride according to the ordinary method and purified as perchlorate. The air-sensitive vanadium(III) complex was prepared using standard Schlenk techniques. Htphpn·$4HClO_4$ (2.57 g; 3 mmol) was dissolved in 30 cm^3 of water and the solution was neutralized by adding NaOH solution. The separated oily material was extracted using chloroform. The chloroform solution was evaporated to dryness and the residue was dissolved in 10 cm^3 of ethanol. This solution was added to the solution of VCl_3 (0.94 g; 6 mmol) in 15 cm^3 of ethanol. To this solution was added the mixture of benzoic acid (0.37 g; 3 mmol) in 10 cm^3 of ethanol and LiOH (0.13 g; 3 mmol) in 5 cm^3 of water. The resulting solution was evaporated to dryness and the residue was redissolved in 50 cm^3 of water. After the undissolved material was filtered off, the filtrate was allowed to stand overnight at room temperature to deposit green crystals.[6]

The structure of the complex was determined using X-ray crystallography.[7] The perspective view of the complex cation is shown in Figure 1 and the selected bond lengths and angles are summarized in the figure caption. The complex cation has a crystallographically forced mirror plane perpendicular to the V···V' axis. The two monomeric units are triply bridged by three different functional groups of the alkoxo group of tphpn, the carboxylato group of the bza, and the hydroxo ligand. We considered that the O2 atom is not an oxide but the oxygen atom of a hydroxide because the charge valence requires one proton per dimeric unit and the V-O2 distance is rather long compared to the V(III)-O^{2-} distance (ca. 1.8 Å).[1,8,9] This consideration is consistent with the fact that a protonation of the bridging oxo group of $[V_2L_2(\mu\text{-}O)(\mu\text{-}C_3H_5O_2)]$ (L = hydridotripyrazolylborate) results in an elongation of the V-O length.[9] This is supported by the fact that the peak in the difference Fourier map appears at 0.846 Å from O2 atom in the direction opposite to O1.

Each vanadium(III) center adopts a heptacoordinate structure.

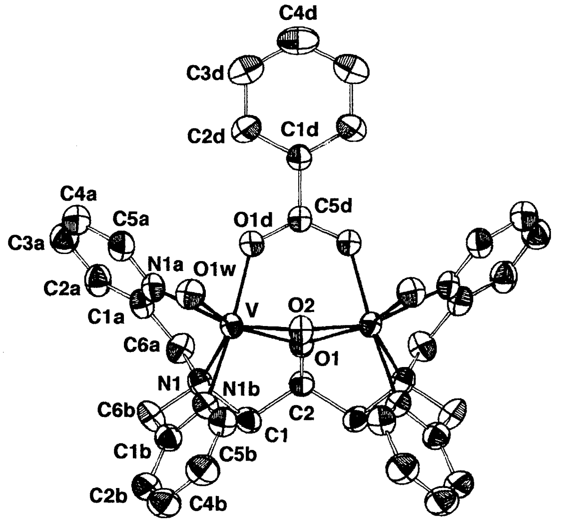

Figure 1. Perspective view of the complex cation. Selected bond distances (Å) and angles (degree) are as follows; V-O1, 2.022 (3); V-O2, 2.023 (3); V-O1d, 2.050 (4); V-O1w, 2.108 (4); V-N1, 2.240 (5); V-N1a, 2.271 (5); V-N1b, 2.191(5); V····V', 3.228 (1); O1-V-O2, 71.7 (2); O1-V-O1d, 86.9 (2); O1-V-N1, 73.9 (2); O1-V-N1a, 119.1 (2); O1-V-N1b, 105.3 (2); O2-V-O1d, 87.0 (2); O2-V-O1w, 83.8 (2); O2-V-N1b, 86.1 (2); O1d-V-O1w, 82.7 (2); O1d-V-N1a, 74.7 (2); O1w-V-N1a, 81.1 (2); O1w-V-N1b, 81.4 (2); N1-V-N1a, 70.2 (2); N1-V-N1b, 71.8 (2); N1a-V-N1b, 107.8 (2); V-O1-V', 105.9(2); V-O2-V', 105.8(2).

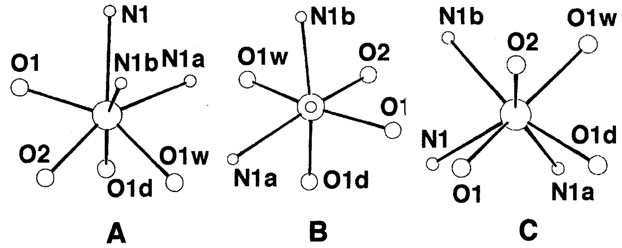

Figure 2. Different views of coordination geometry: A, capped octahedron; B, view from V-N1 axis; C, square base-trigonal cap

As indicated in Figure 2, the heptacoordinate structure can be described as a distorted capped octahedron or alternatively as a square base-trigonal cap polyhedron. A capped octahedron can be characterized by two sets of spherical angles;[10] in the present case, N1-V-O1, N1-V-N1b, and N1-V-N1a angles and N1-V-O2, N1-V-O1d, and N1-V-O1w angles. The average angle of these two sets are 72.0° and 129.0°. These angles are not very different from 75° and 130° which were calculated as the optimum angles for a capped octahedron from the molecular orbital treatment, and are within the range of the observed values for other d^2 complexes having a capped octahedral structure.[10]

In the manganese complex containing an alkoxo bridge of tphpn and a carboxylato bridge,[11] the $N(CH_2\text{-}py)_2$ moiety of the tphpn coordinates in a meridional fashion. This meridional coordination leaves a free coordination site trans to the alkoxo oxygen atom, which resulted in a further aggregation to a tetramer, $[Mn_4(tphpn)_2(CH_3COO)_2(O)(H_2O)_2]^{4+}$. In the present vanadium(III) complex, the $N(CH_2\text{-}py)_2$ moiety takes a facial coordination, which can prevent the formation of such a tetramer as that found for the manganese complex. The facial coordination of the $N(CH_2\text{-}py)_2$ moiety has been found in $[(Mn_2O_2)_2(tphpn)_2]^{4+}$ that has no carboxylato bridge.[12]

The V-N(pyridyl and amino) distances in the present complex are slightly longer than those found in $[V_2(O)Br_2(tpa)_2]Br_2$[13] (tpa = trispyridylmethylamine), reflecting the heptacoordinate structure. The V-O(alkoxo and carboxylato) distances are also elongated compared to those found in $[V_2(dpot)(m\text{-}hbza)(H_2O)_2]$ (hbza = hydroxybenzoate).[14]

References and Notes

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6 Yield, 1.53 g. Anal. Calcd for $[V_2(bza)(OH)(tphpn)(H_2O)_2]Cl_3 \cdot 8H_2O = C_{34}H_{55}N_6O_{14}Cl_3V_2$: C, 41.67; H, 5.66; N, 8.57 %. Found: C, 41.47; H, 5.81; N, 8.50 %.

7 Crystal data: formula, $V_2C_{34}H_{39}N_6O_6Cl_3 \cdot 8H_2O$; fw, 973.78; space group, *Pbcm* (No.57); $a = 10.546(1)$ Å, $b = 18.898(2)$ Å, $c = 22.333(1)$ Å; $Z = 4$; $D_{calcd} = 1.45$; R (Rw) = 0.077 (0.079). A total of 3528 independent reflections with $|Fo|>3\sigma(Fo)$ were used for the calculation. One crystalline water molecule was disordered in four positions.

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